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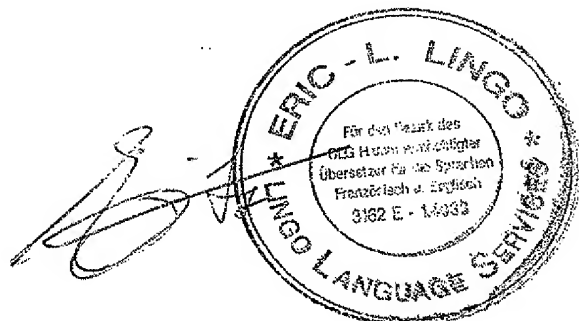
Patent specifications: German Patent Application No. 102 46 461.8  
(Claims / Description / Abstract)

Title: DE: Protonenleitende Polymembran enthaltend Polyazolblends  
und deren Anwendung in Brennstoffzellen

EN: Proton-conducting polymer membrane comprising polyazole  
blends and its application in fuel cells

Applicant: Celanese Ventures GmbH, Frankfurt am Main/DE

Place, date: Dortmund, 10. June 2009



# **FEDERAL REPUBLIC OF GERMANY**

## **Certification of priority for the filing of a patent application**

**File number:** 102 46 461.8

**Application date:** 4<sup>th</sup> October 2002

**Applicant/Owner:** Celanese Ventures GmbH Frankfurt/Main, Germany

**Title:** Proton-conducting polymer membrane comprising  
polyazole blends and its application in fuel cells

**IPC:** B 01 D, H 01 M

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Munich, 23<sup>rd</sup> October 2003

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Wehne

Proton-conducting polymer membrane comprising polyazole blends and its application in fuel cells

The present invention relates to a proton-conducting polymer electrolyte membrane comprising polyazole blends and can, owing to its excellent chemical and thermal properties, be used for a variety of purposes, in particular as polymer electrolyte membrane (PEM) in so called PEM fuel cells.

A fuel cell usually comprises an electrolyte and two electrodes separated by the electrolyte. In the case of a fuel cell, a fuel such as hydrogen gas or a methanol/water mixture is supplied to one of the two electrodes and an oxidant such as oxygen gas or air is supplied to the other electrode and chemical energy from the oxidation of the fuel is in this way converted directly into electric energy. In the oxidation reaction protons and electrons are formed.

The electrolyte is permeable to hydrogen ions, i.e. protons, but not to reactive fuels such as the hydrogen gas or methanol and the oxygen gas.

As a rule, a fuel cell has a plurality of single cells known as MEUs (membrane-electrode units), each of which comprises an electrolyte and two electrodes separated by the electrolyte.

Electrolytes employed for the fuel cell are solids such as polymer electrolyte membranes or liquids such as phosphoric acid. Recently, polymer electrolyte membranes have attracted attention as electrolytes for fuel cells. In principle, a distinction can be made between two categories of polymer membranes.

The first category encompasses cation-exchange membranes comprising a polymer framework containing covalently bound acid groups, preferably sulphonic acid groups. The sulphonic acid group is converted into an anion releasing a hydrogen ion and therefore conducts protons. The mobility of the proton and thus the proton conductivity is linked directly to the water content. Due to the very good miscibility of methanol and water, such cation-exchange membranes have high methanol permeability and are therefore unsuited for application in a direct methanol fuel cell. If the membrane dries, e.g. as a result of high temperature, the conductivity of the membrane and consequently the power of the fuel cell

decrease considerably. The operating temperatures of fuel cells containing such cation-exchange membranes are thus limited to the boiling point of water. Moistening of the fuels represents a great technical challenge for the use of polymer electrolyte membrane fuel cells (PEMFCs) in which conventional, sulphonated membranes such as Nafion are used.

Thus, for example, perfluorosulphonic acid polymers are materials used for polymer electrolyte membranes. The perfluorosulphonic acid polymer (e.g. Nafion) generally has a perfluorinated hydrocarbon skeleton such as a copolymer of tetrafluoroethylene and trifluorovinyl and a side chain bearing a sulphonic acid group, e.g. a side chain bearing a sulphonic acid group bound to a perfluoroalkylene group, bound thereto.

The cation-exchange membranes are preferably organic polymers having covalently bound acid groups, in particular sulphonic acid. Processes for the sulfonation of polymers are described in F. Kucera et al., Polymer Engineering and Science 1988, Vol. 38, No. 5, 783-792.

The most important types of cation-exchange membranes which have achieved commercial importance for use in fuel cells are listed below:

The most important representative is the perfluorosulphonic acid polymer Nafion® (US 3692569). This polymer can be brought into solution and then used as ionomer, as described in US 4453991. Cation-exchange membranes are also obtained by filling a porous carrier material with such an ionomer. As carrier material, preference is given to expanded Teflon (US 5635041). A further perfluorinated cation-exchange membrane can be produced by copolymerization of trifluorostyrene and sulphonyl-modified trifluorostyrene, as described in US5422411. Composite membranes comprising a porous carrier material, in particular expanded Teflon, filled with ionomers consisting of such sulphonyl-modified trifluorostyrene copolymers are described in US5834523.

US6110616 describes copolymers of butadiene and styrene and their subsequent sulfonation to produce cation-exchange membranes for fuel cells.

A further class of partially fluorinated cation-exchange membranes can be

produced by radiation grafting and subsequent sulfonation. Here, a grafting reaction, preferably using styrene, is carried out on a previously radiated polymer film as described in EP667983 or DE19844645. The side chains are then sulfonated in a subsequent sulfonation reaction. A cross linking reaction can also  
5 be carried out simultaneously with the grafting reaction and the mechanical properties can be altered in this manner.

Apart from the above membranes, a further class of nonfluorinated membranes produced by sulfonating high-temperature stable thermoplastics has been developed. Thus, membranes composed of sulfonated polyether ketones  
10 (DE4219077, EP96/01177), sulfonated polysulfone (J. Membr. Sci. 83 (1993) p. 211) or sulfonated polyphenylene sulfide (DE19527435) are known.

Ionomers prepared from sulfonated polyether ketones are described in WO 00/15691.

Furthermore, acid-base blend membranes are known, which are produced by  
15 mixing sulfonated polymers and basic polymers, as described in DE19817374 or WO 01/18894.

To further improve the membrane properties, a cation-exchange membrane known from the prior art can be mixed with a high-temperature stable polymer. The production and properties of cation-exchange membranes consisting of blends of  
20 sulfonated PEK and a) polysulfones (DE4422158), b) aromatic polyamides (42445264) or c) polybenzimidazole (DE19851498) have been described.

However, a problem associated with such membranes is their complicated and thus expensive production, since it is usual firstly to form various polymers which are subsequently cast, frequently with the aid of a solvent, to produce a film. To  
25 prepare the sulfonated polymers, the PEK is usually dissolved in a suitable solvent and subsequently reacted with an aggressive sulfonating reagent, for example oleum or chlorosulfonic acid. This reaction is relatively critical, since the sulfonating reagent is a strong oxidizing agent so that degradation of the PEK cannot be ruled out. This would, in particular, have an adverse effect on the  
30 mechanical properties of the polymer. The sulfonated polymer is isolated and converted into the neutral form in a further process step. The polymer is then

brought into solution again. A polymer film can, inter alia, be cast from this solution. The solvent used for this purpose, for example N-dimethylacetamide, subsequently has to be removed. Accordingly, the process for producing such membranes is complicated and therefore expensive.

- 5    Uncontrolled sulfonation at many points on the polymer takes place in the sulfonation processes using very strong sulfonating agents. The sulfonation can also lead to chain rupture and thus to a worsening of the mechanical properties and finally to premature failure of the fuel cells.

10    Sulfonated polybenzimidazoles are also known from the literature. Thus, US-A-4634530 describes sulfonation of an undoped polybenzimidazole film by means of a sulfonating agent such as sulfuric acid or oleum in the temperature range up to 100°C.

15    Furthermore, Staiti et al. (P. Staiti in J. Membr. Sci. 188 (2001) 71) have described the preparation and properties of sulfonated polybenzimidazoles. It was in this case not possible to carry out the sulfonation on the polymer in the solution. Addition of the sulfonating agent to the PBI/DMAc solution results in precipitation of the polymer. To carry out the sulfonation, a PBI film was produced first and this was dipped into a dilute sulfuric acid. The samples were then treated at temperatures of about 475°C for 2 minutes to effect sulfonation. The sulfonated  
20    PBI membranes have a maximum conductivity of only  $7.5 \cdot 10^{-5}$  S/cm at a temperature of 160°C.

25    The production of sulfoalkylated PBI membranes by reacting a hydroxyethyl-modified PBI with a sultone is described in US-A-4997892. On the basis of this technology, it is possible to produce sulfopropylated PBI membranes (Sanui et al. in Polym. Adv. Techn. 11 (2000) 544). The proton conductivity of such membranes is  $10^{-3}$  S/cm and is thus too low for use in fuel cells in which 0.1 S/cm is sought.

30    A disadvantage of all these cation-exchange membranes is the fact that the membrane has to be moistened, the operating temperature is limited to 100°C and the membranes have a high methanol permeability. The reason for these disadvantages is the conductivity mechanism of the membrane, in which the transport of the protons is coupled to the transport of the water molecule. This is

referred to as the "vehicle mechanism" (K.-D. Kreuer, Chem. Mater. 1996, 8, 610-641).

As a second category, polymer electrolyte membranes comprising complexes of basic polymers and strong acids have been developed. Thus, WO 96/13872 and the corresponding US patent 5,525,436 describe a process for producing a proton-conducting polymer electrolyte membrane, in which a basic polymer such as polybenzimidazole is treated with a strong acid such as phosphoric acid, sulfuric acid, etc.

*J. Electrochem. Soc.*, volume 142, No. 7, 1995, pp. L121-L123, describes doping of a polybenzimidazole in phosphoric acid.

In the case of the basic polymer membranes known from the prior art, the mineral acid used for achieving the required proton conductivity (usually concentrated phosphoric acid) is usually added to the polyazole film after shaping. The polymer in this case serves as support for the electrolyte comprising the highly concentrated phosphoric acid. The polymer membrane performs further important functions; in particular, it has to have a high mechanical stability and serve as separator for the two fuels mentioned above.

A significant advantage of such a membrane doped with phosphoric acid is the fact that a fuel cell in which such a polymer electrolyte membrane is used can be operated at temperatures above 100°C without the moistening of the fuels which is otherwise necessary. This is due to the ability of phosphoric acid to transfer protons without additional water by means of the Grotthuss mechanism (K.-D. Kreuer, Chem. Mater. 1996, 8, 610-641).

The possibility of operation at temperatures above 100°C results in further advantages for the fuel cell system. Firstly, the sensitivity of the Pt catalyst to impurities in the gas, in particular CO, is greatly reduced. CO is formed as by-product in the reforming of the hydrogen-rich gas comprising hydrocarbon-containing compounds, e.g. natural gas, methanol or petroleum spirit, or as intermediate in the direct oxidation of methanol. The CO content of the fuel typically has to be less than 100 ppm at temperatures of <100°C. However, at temperatures in the range 150-200°, 10 000 ppm or more of CO can also be

tolerated (N.J. Bjerrum et al. Journal of Applied Electrochemistry, 2001, 31, 773-779). This leads to significant simplifications of the upstream reforming process and thus to cost reductions for the total fuel cell system.

5 A great advantage of fuel cells is the fact that the electrochemical reaction converts the energy of the fuel directly into electric energy and heat. Water is formed as reaction product at the cathode. Heat is thus generated as by-product in the electrochemical reaction. In the case of applications in which only the electric power is utilized for driving electric motors, e.g. in automobile applications, or as replacement for battery systems in many applications, the heat has to be removed  
10 in order to avoid overheating of the system. Additional, energy-consuming equipment is then necessary for cooling, and this further reduces the total electrical efficiency of the fuel cell. In the case of stationary applications such as central or decentralized generation of power and heat, the heat can be utilized efficiently by means of existing technologies, e.g. heat exchangers. High  
15 temperatures are sought here to increase the efficiency. If the operating temperature is above 100°C and the temperature difference between ambient temperature and the operating temperature is large, it is possible to cool the fuel cell system more efficiently or employ small cooling areas and dispense with additional equipment compared to fuel cells which have to be operated at below  
20 100°C because of the moistening of the membrane.

However, besides these advantages, such a fuel cell system also has disadvantages. Thus, the durability of the membranes doped with phosphoric acid is relatively limited. The life is, in particular, significantly reduced by operation of the fuel cell at below 100°C, for example at 80°C. However, it needs to be noted in  
25 this regard that the cell has to be operated at these temperatures on start-up and shutdown of the fuel cell.

Furthermore, the production of membranes doped with phosphoric acid is relatively expensive since it is usual firstly to form a polymer which is subsequently cast with the aid of a solvent to produce a film. After the film has been dried, it is doped with  
30 an acid in a final step. The polymer membranes known hitherto therefore have a high concentration of dimethylacetamide (DMAc) which cannot be removed completely by means of known drying methods.



In addition, the performance, for example the conductivity, of known membranes is in need of improvement.

Furthermore, the mechanical stability of known high-temperature membranes having a high conductivity is in need of improvement.

5 It is therefore an object of the present invention to provide a novel polymer electrolyte membrane which achieves the abovementioned objects. Another object of the present invention is to provide polymer electrolyte membranes which have good performance, in particular a high conductivity over a wide temperature range. Here, the conductivity should, in particular at high temperatures, be achieved  
10 without additional moistening. The membrane should have a high mechanical stability relative to its performance.

Furthermore, the operating temperature should be able to be extended to the range from  $<80^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  without the life of the fuel cell being greatly reduced.

15 These objects are achieved by a proton-conducting polymer membrane comprising polyazole blends and having all the features of claim 1.

A membrane according to the invention displays a high conductivity over a wide temperature range and this is achieved even without additional moistening. A membrane according to the invention displays a relatively high mechanical stability. Furthermore, a membrane according to the invention can be produced  
20 simply and inexpensively. Thus, in particular, large amounts of expensive solvents such as dimethylacetamide can be dispensed with.

Furthermore, these membranes have a surprisingly long life. In addition, a fuel cell equipped with a membrane according to the invention can also be operated at low temperatures, for example at  $80^{\circ}\text{C}$ , without the life of the fuel cell being greatly  
25 reduced thereby.

The present invention provides a proton-conducting polymer membrane which comprises polyazole blends and is obtainable by a process comprising the steps

A) preparation of a mixture comprising

polyphosphoric acid,

at least one polyazole (polymer A) and/or one or more compounds which are suitable for forming polyazoles under the action of heat according to step B),

5 B) heating of the mixture obtainable according to step A) under inert gas to temperatures of up to 400°C,

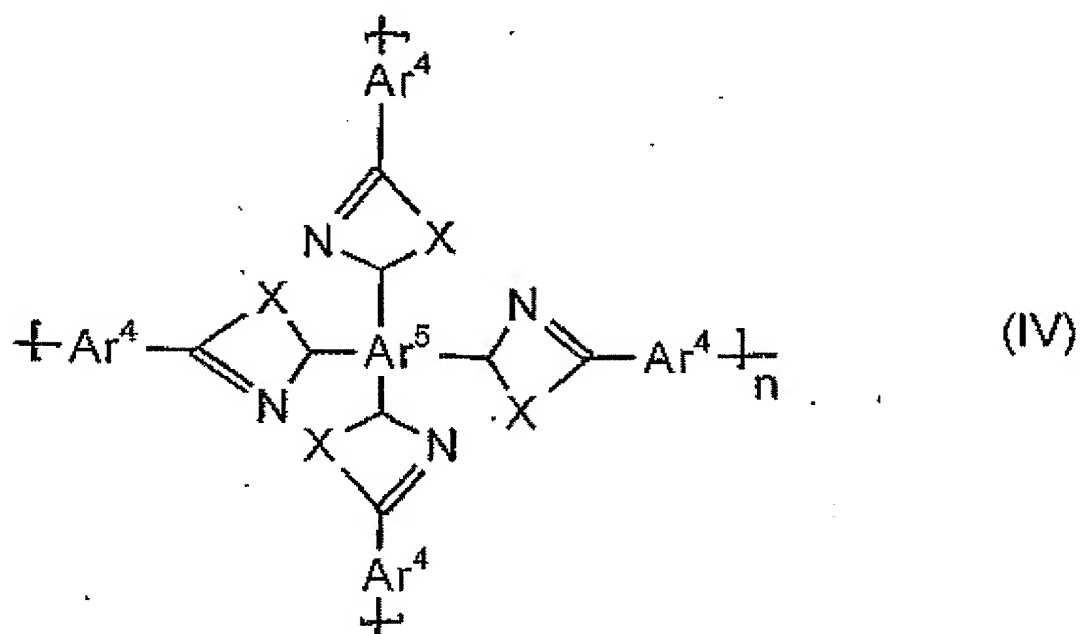
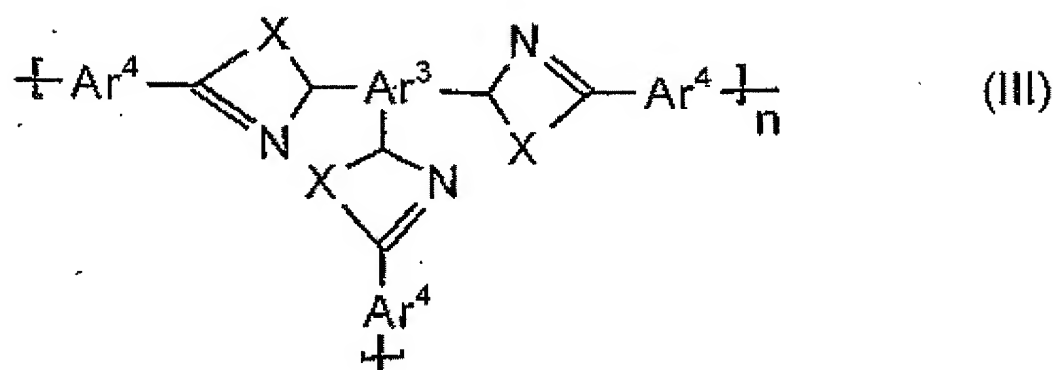
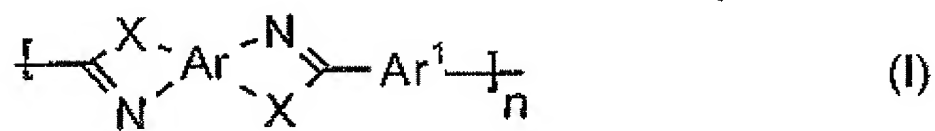
C) application of a layer using the mixture from step A) and/or B) to a support,

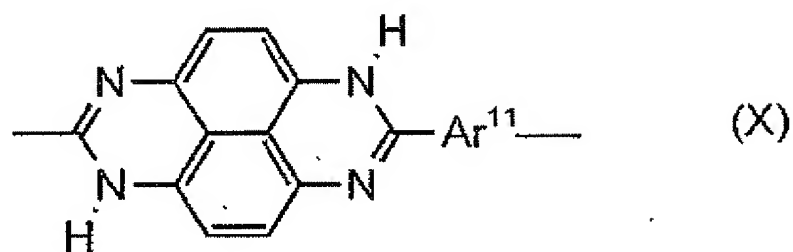
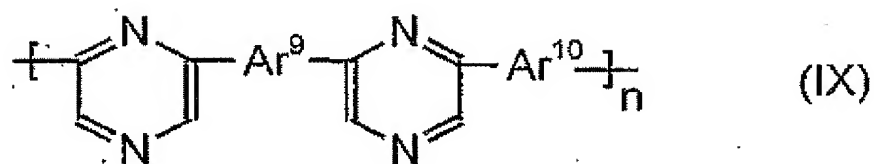
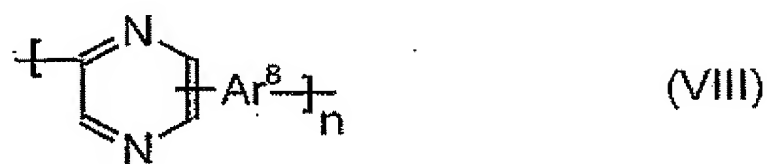
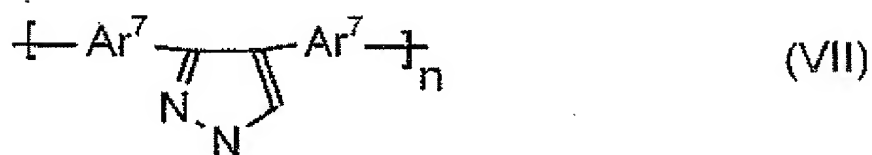
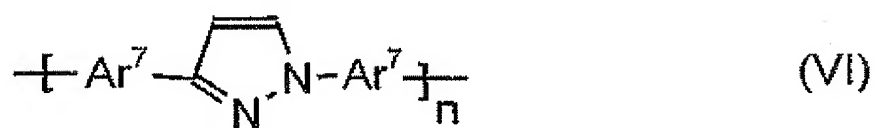
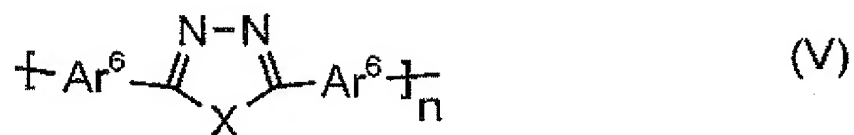
D) treatment of the membrane formed in step C) until it is self-supporting,

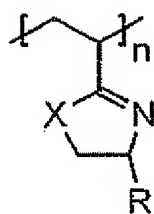
10 with at least one further polymer (polymer B) which is not a polyazole being added to the composition obtainable according to step A) and/or step B) and the weight ratio of polyazole to polymer B is in the range from 0.1 to 50.

15 The composition prepared according to step B) comprises polyazoles. These polymers can be added already in step A). Moreover, these polymers can also be obtained from the monomers, oligomers and/or prepolymers on which the polymer is based during the heating in step B).

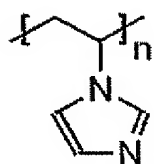
20 Polymers based on polyazole comprise recurring azole units of the general formula (I) and/or (II) and/or (III) and/or (IV) and/or (V) and/or (VI) and/or (VII) and/or (VIII) and/or (IX) and/or (X) and/or (XI) and/or (XII) and/or (XIII) and/or (XIV) and/or (XV) and/or (XVI) and/or (XVII) and/or (XVIII) and/or (XIX) and/or (XX) and/or (XXI) and/or (XXII)



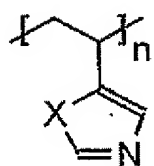




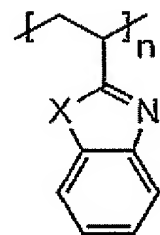
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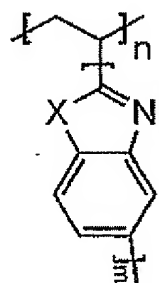
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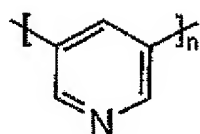
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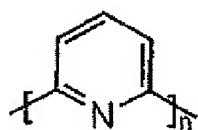
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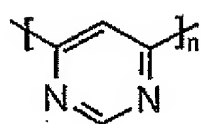
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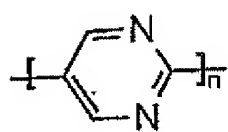
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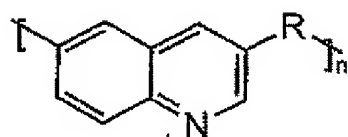
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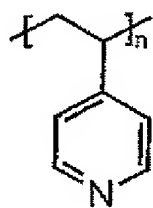
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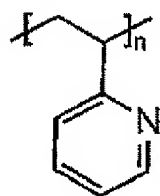
(XIX)



(XX)



(XXI)



(XXII)

wherein

- Ar are identical or different and represent a tetravalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,
- 5 Ar<sup>1</sup> are identical or different and represent a bivalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,
- Ar<sup>2</sup> are identical or different and represent a bivalent or trivalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,
- Ar<sup>3</sup> are identical or different and represent a trivalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,
- 10 Ar<sup>4</sup> are identical or different and represent a trivalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,
- Ar<sup>5</sup> are identical or different and represent a tetravalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,
- 15 Ar<sup>6</sup> are identical or different and represent a bivalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,
- Ar<sup>7</sup> are identical or different and represent a bivalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,
- Ar<sup>8</sup> are identical or different and represent a trivalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,
- 20 Ar<sup>9</sup> are identical or different and represent a bivalent or trivalent or tetravalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,
- Ar<sup>10</sup> are identical or different and represent a bivalent or trivalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,
- 25 Ar<sup>11</sup> are identical or different and represent a bivalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

X are identical or different and represent oxygen, sulphur or an amino group which carries a hydrogen atom, a group having 1 - 20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as a further radical,

5 R are identical or different and are each hydrogen, an alkyl group or an aromatic group and

n, m are each an integer greater than or equal to 10, preferably greater than or equal to 100.

Preferred aromatic or heteroaromatic groups are derived from benzene,  
10 naphthalene, biphenyl, diphenyl ether, diphenylmethane, diphenyldimethylmethane, bisphenone, diphenyl sulfone, thiophene, furan, pyrrole, thiazole, oxazole, imidazole, isothiazole, isoxazole, pyrazole, 1,3,4-oxadiazole, 2,5-diphenyloxadiazole, 1,3,4-thiadiazole, 1,3,4-triazole, 2,5-diphenyl-1,3,4-triazole, 1,2,5-triphenyl-1,3,4-triazole, 1,2,4-oxadiazole, 1,2,4-thiadiazole,  
15 1,2,4-triazole, 1,2,3-triazole, 1,2,3,4-tetrazole, benzo[b]thiophene, benzo[b]furan, indole, benzo[c]thiophene, benzo[c]furan, isoindole, benzoxazole, benzothiazole, benzimidazole, benzisoxazole, benzisothiazole, benzopyrazole, benzothiadiazole, benzotriazole, dibenzofuran, dibenzothiophene, carbazole, pyridine, bipyridine, pyrazine, pyrazole, pyrimidine, pyridazine, 1,3,5-triazine, 1,2,4-triazine,  
20 1,2,4,5-triazine, tetrazine, quinoline, isoquinoline, quinoxaline, quinazoline, cinnoline, 1,8-naphthyridine, 1,5-naphthyridine, 1,6-naphthyridine, 1,7-naphthyridine, phthalazine, pyridopyrimidine, purine, pteridine or quinolizine, 4H-quinolizine, diphenyl ether, anthracene, benzopyrrole, benzoxathiadiazole, benzoxadiazole, benzopyridine, benzopyrazine, benzopyrazidine,  
25 benzopyrimidine, benzotriazine, indolizine, pyridopyridine, imidazopyrimidine, pyrazinopyrimidine, carbazole, acridine, phenazine, benzoquinoline, phenoxazine, phenothiazine, acridine, benzopteridine, phenanthroline and phenanthrene, which may also be substituted.

In this case, Ar<sup>1</sup>, Ar<sup>4</sup>, Ar<sup>6</sup>, Ar<sup>7</sup>, Ar<sup>8</sup>, Ar<sup>9</sup>, Ar<sup>10</sup>, Ar<sup>11</sup> can have any substitution pattern,  
30 in the case of phenylene, for example, Ar<sup>1</sup>, Ar<sup>4</sup>, Ar<sup>6</sup>, Ar<sup>7</sup>, Ar<sup>8</sup>, Ar<sup>9</sup>, Ar<sup>10</sup>, Ar<sup>11</sup> can be ortho-phenylene, meta-phenylene and para-phenylene. Particularly preferred



groups are derived from benzene and biphenylene which may also be substituted.

Preferred alkyl groups are short-chain alkyl groups having from 1 to 4 carbon atoms, such as, e.g., methyl, ethyl, n-propyl or i-propyl and t-butyl groups.

Preferred aromatic groups are phenyl or naphthyl groups. The alkyl groups and  
5 the aromatic groups may be substituted.

Preferred substituents are halogen atoms, e.g. fluorine, amino groups, hydroxy groups or short-chain alkyl groups, e.g. methyl or ethyl groups.

Preference is given to polyazoles having recurring units of the formula (I) in which the radicals X within one recurring unit are identical.

10 The polyazoles can in principle also have different recurring units wherein their radicals X are different, for example. However, there are preferably only identical radicals X in a recurring unit.

Further preferred polyazole polymers are polyimidazoles, polybenzothiazoles, polybenzoxazoles, polyoxadiazoles, polyquinoxalines, polythiadiazoles,  
15 poly(pyridines), poly(pyrimidines) and poly(tetrazapyrenes).

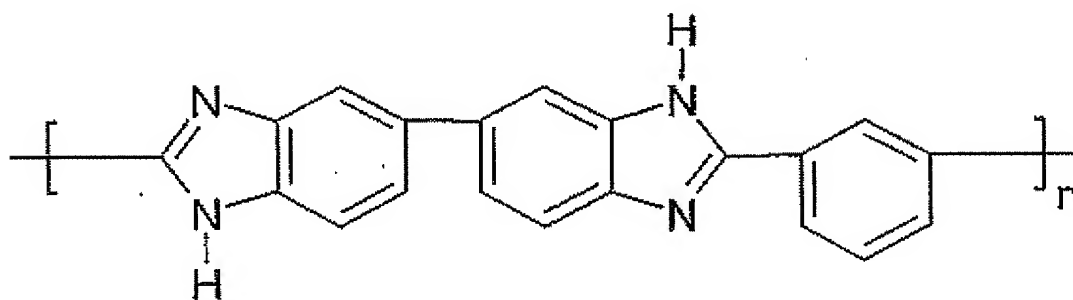
In another embodiment of the present invention, the polymer containing recurring azole units is a copolymer or a blend which contains at least two units of the formulae (I) to (XXII) which differ from one another. The polymers can be in the form of block copolymers (diblock, triblock), random copolymers, periodic  
20 copolymers and/or alternating polymers.

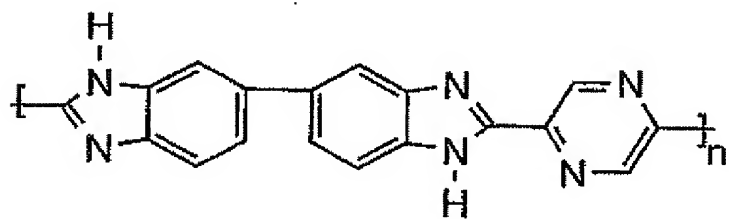
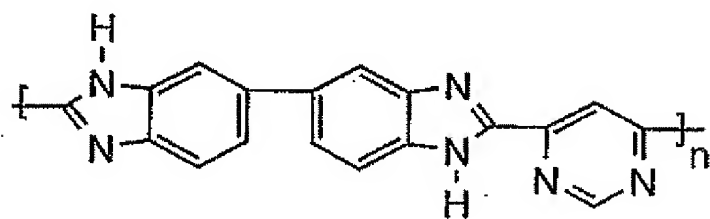
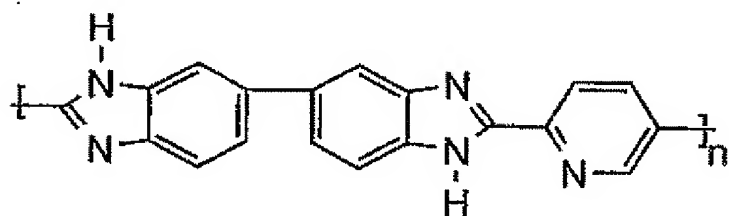
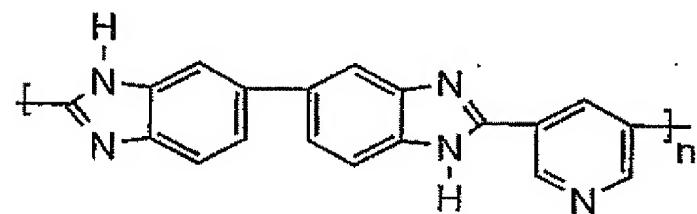
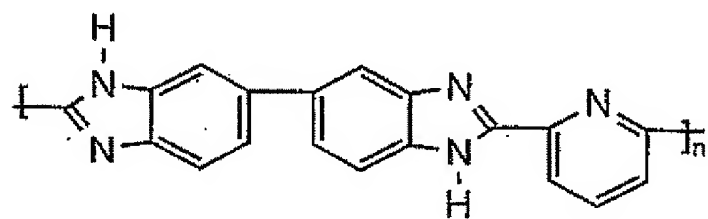
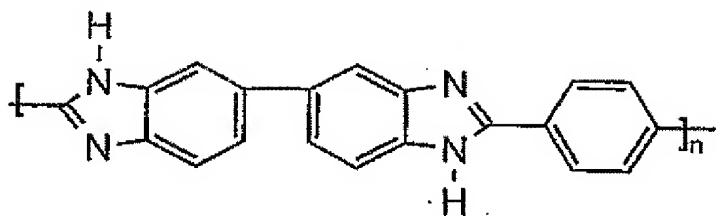
In a particularly preferred embodiment of the present invention, the polymer containing recurring azole units is a polyazole, which only contains units of the formulae (I) and/or (II).

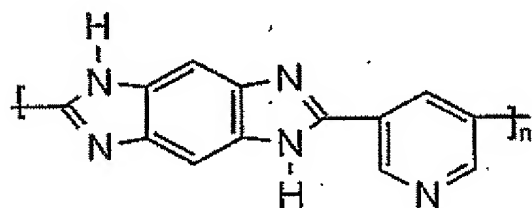
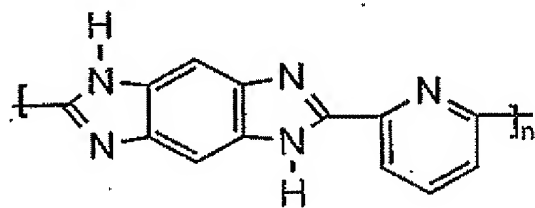
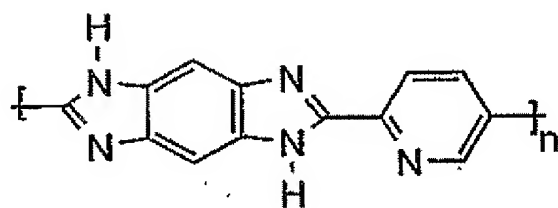
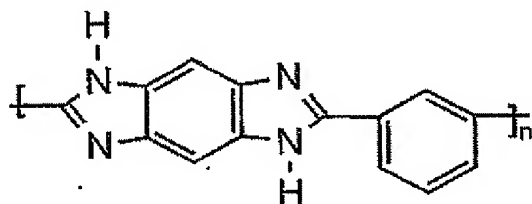
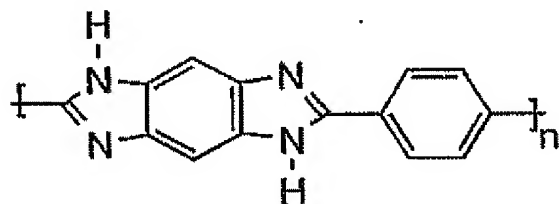
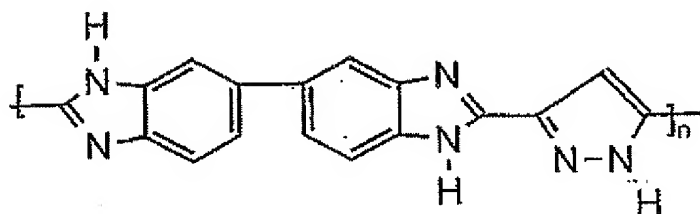
The number of recurring azole units in the polymer is preferably an integer greater  
25 than or equal to 10. Particularly preferred polymers contain at least 100 recurring azole units.

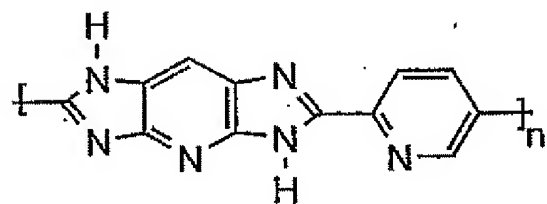
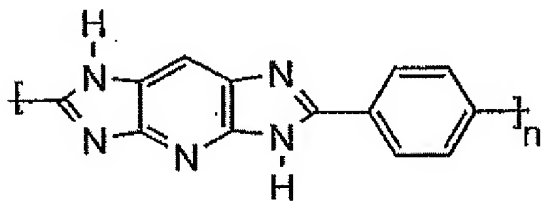
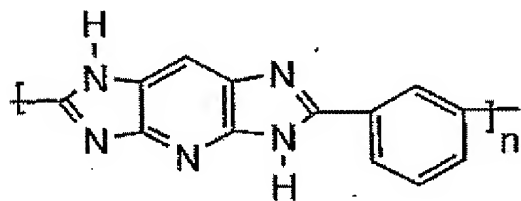
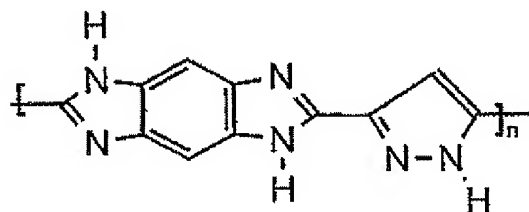
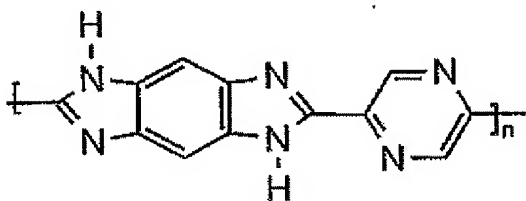
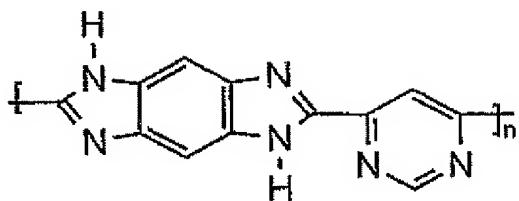
Within the context of the present invention, preference is given to polymers containing recurring benzimidazole units. Some examples of the most appropriate

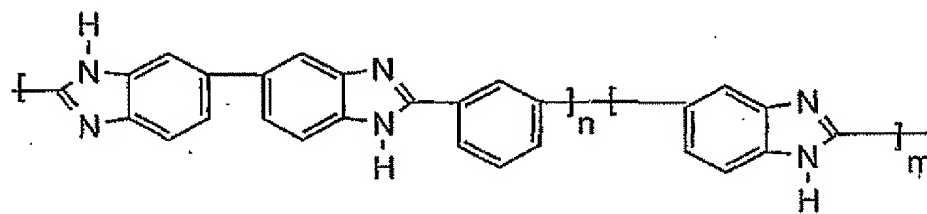
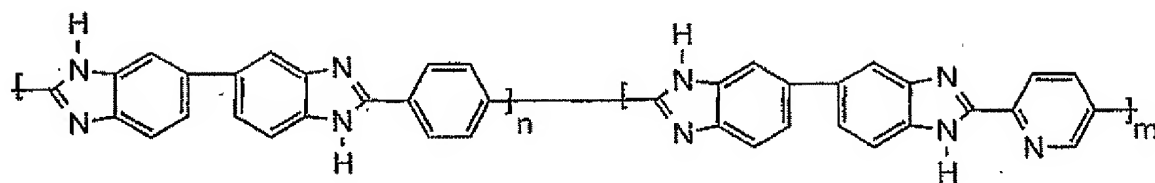
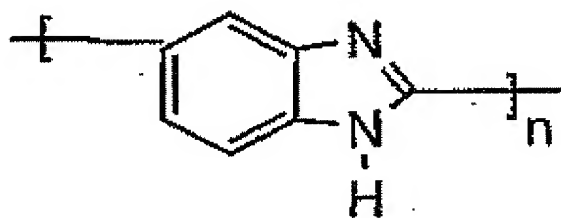
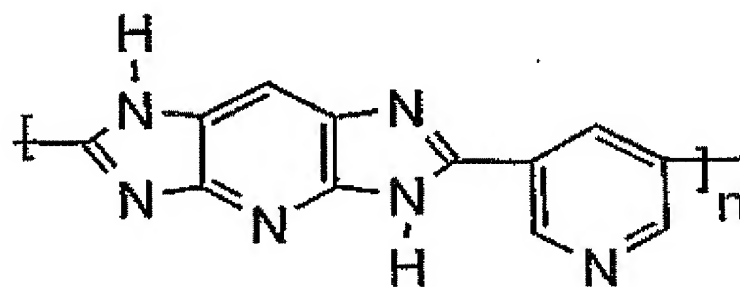
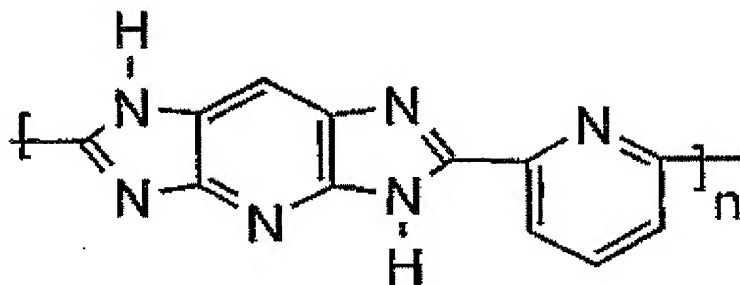
polymers containing recurring benzimidazole units are represented by the following formulae:











where  $n$  and  $m$  are each an integer greater than or equal to 10, preferably greater

than or equal to 100.

The polyazoles used in step A), but in particular the polybenzimidazoles, have a high molecular weight. Measured as intrinsic viscosity, it is preferably in the range from 0.3 to 10 dl/g, in particular from 1 to 5 dl/g.

- 5 Furthermore, the polyazoles can also be prepared by heating in step B). For this purpose, one or more compounds which are suitable for forming polyazoles under the action of heat according to step B) can be added to the mixture in step A).

Mixtures comprising one or more aromatic and/or heteroaromatic tetraamino compounds and one or more aromatic and/or heteroaromatic carboxylic acids or  
10 derivatives thereof which have at least two acid groups per carboxylic acid monomer are suitable for this purpose. It is also possible to use one or more aromatic and/or heteroaromatic diaminocarboxylic acids for the preparation of polyazoles.

The aromatic and heteroaromatic tetraamino compounds include, inter alia,  
15 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine, 1,2,4,5-tetraaminobenzene, bis(3,4-diaminophenyl)sulfone, bis(3,4-diaminophenyl) ether, 3,3',4,4'-tetraaminobenzophenone, 3,3',4,4'-tetraaminodiphenylmethane and 3,3',4,4'-tetraaminodiphenyldimethylmethane and their salts, in particular their monohydrochloride, dihydrochloride, trihydrochloride and tetrahydrochloride  
20 derivatives. Among these, 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine and 1,2,4,5-tetraaminobenzene are particularly preferred.

Furthermore, the mixture A) can comprise aromatic and/or heteroaromatic carboxylic acids. These are dicarboxylic acids, tricarboxylic acids and tetracarboxylic acids or their esters or their anhydrides or their acid halogenides, in  
25 particular their acid halogenides and/or acid bromides. Preferably, the aromatic dicarboxylic acids are isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,6-  
30 dihydroxyisophthalic acid, 4,6-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid,

5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, diphenyl ether-4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid, diphenylsulphone-4,4'-dicarboxylic acid, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid or their C1-C20 alkyl esters or C5-C12 aryl esters or their acid anhydrides or their acid chlorides.

The aromatic tricarboxylic acids or their C1-C20 alkyl esters or C5-C12 aryl esters or their acid anhydrides or their acid chlorides are preferably 1,3,5-benzenetricarboxylic acid (trimesic acid), 1,2,4-benzenetricarboxylic acid (trimellitic acid),

(2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphenyltricarboxylic acid, 3,5,4'-biphenyltricarboxylic acid.

The aromatic tetracarboxylic acids or their C1-C20-alkyl esters, C5-C12-aryl esters or their acid anhydrides or their acid chlorides are preferably 3,5,3',5'-biphenyltetracarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid, 1,4,5,8-naphthalenetetracarboxylic acid.

The heteroaromatic carboxylic acids are heteroaromatic dicarboxylic acids and tricarboxylic acids and tetracarboxylic acids or their esters or their anhydrides. For the purposes of the present invention, heteroaromatic carboxylic acids are aromatic systems in which at least one nitrogen, oxygen, sulfur or phosphorus atom is present in the aromatic. Preferably, these are pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid and their C1-C20



alkyl esters or C5-C12 aryl esters or their acid anhydrides or their acid chlorides.

The content of tricarboxylic acids or tetracarboxylic acids (based on dicarboxylic acid used) is in the range from 0 to 30 mol%, preferably from 0.1 to 20 mol%, in particular from 0.5 to 10 mol%.

- 5 Furthermore, the mixture A) can also comprise aromatic and heteroaromatic diaminocarboxylic acids. These include, inter alia, diaminobenzoic acid, 4-phenoxycarbonylphenyl-3',4'-diaminophenyl ether and their monochloride and dihydrochloride derivatives.

- 10 Preferably, mixtures of at least 2 different aromatic carboxylic acids are used in step A). Particularly preferably, mixtures are used which also contain heteroaromatic carboxylic acids additional to aromatic carboxylic acids. The mixing ratio of aromatic carboxylic acids to heteroaromatic carboxylic acids is between 1:99 and 99:1, preferably 1:50 and 50:1.

- 15 These mixtures are, in particular, mixtures of N-heteroaromatic dicarboxylic acids and aromatic dicarboxylic acids. Non-limiting examples of dicarboxylic acids are isophthalic acid, terephthalic acid, phthalic acid, 2,5-dihydroxyterephthalic acid, 2,6-dihydroxyisophthalic acid, 4,6-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, diphenyl ether-4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid, diphenylsulphone-4,4'-dicarboxylic acid, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid.
- 20
- 25

- If a very high molecular weight is to be achieved, the molar ratio of carboxylic acid groups to amino groups in the reaction of tetraamino compounds with one or more aromatic carboxylic acids or esters thereof having at least two acid groups per carboxylic acid monomer is preferably in the vicinity of 1:2.
- 30

The mixture prepared in step A) preferably comprises at least 0.5% by weight, in particular from 1 to 30% by weight and particularly preferably from 2 to 15% by weight, of monomers for the preparation of polyazoles.

5 If the polyazoles are prepared from the monomers directly in the polyphosphoric acid, the polyazoles have a high molecular weight. This applies particularly to the polybenzimidazoles. Measured as intrinsic viscosity, it is in the range from 0.3 to 10 dl/g, preferably from 1 to 5 dl/g.

If the mixture in accordance with step A) also contains tricarboxylic acids or tetracarboxylic acid, branching/cross-linking of the formed polymer is achieved  
10 therewith. This contributes to an improvement in the mechanical property.

In a further embodiment of the present invention, the mixture prepared in step A) comprises compounds which are suitable for forming polyazoles under the action of heat in step B) these compounds can be obtained by reaction of one or more aromatic and/or heteroaromatic tetraamino compounds with one or more aromatic  
15 and/or heteroaromatic carboxylic acids or derivatives thereof containing at least two acid groups per carboxylic acid monomer or of one or more aromatic and/or heteroaromatic diaminocarboxylic acids in the melt at temperatures of up to 400°C, in particular up to 350°C, preferably up to 280°C. The compounds to be used for preparing these prepolymers have been described above.

20 The polyphosphoric acid used in step A) is a commercial polyphosphoric acid as can be obtained, for example, from Riedel-de Haen. The polyphosphoric acids  $H_{n+2}P_nO_{3n+1}$  ( $n > 1$ ) usually have a concentration of at least 83%, calculated as  $P_2O_5$  (by acidimetry). Instead of a solution of the monomers, it is also possible to produce a dispersion/suspension.

25 According to the invention, at least one further polymer which is not a polyazole (polymer B) is added to the composition produced in step A) and/or step B). This polymer can be present, inter alia, in dissolved, dispersed or suspended form.

Here, the weight ratio of polyazole to polymer (B) is in the range from 0.1 to 50, preferably from 0.2 to 20, particularly preferably from 1 to 10. If the polyazole is not  
30 formed until step B), the weight ratio can be calculated from the weight of the

monomers for forming the polyazole, taking the compounds released in the condensation, for example water, into account.

- Preferred polymers include, inter alia, polyolefins such as poly(chloroprene), polyacetylene, polyphenylene, poly(*p*-xylylene), polyarylmethylene, polyarmethylene, polystyrene, polymethylstyrene, polyvinyl alcohol, polyvinyl acetate, polyvinyl ether, polyvinylamine, poly(N-vinylacetamide), polyvinylimidazole, polyvinylcarbazole, polyvinylpyrrolidone, polyvinylpyridine, polyvinyl chloride, polyvinylidene chloride, polytetrafluoroethylene, polyhexafluoropropylene, copolymers of PTFE with hexafluoropropylene, with perfluoropropyl vinyl ether, with trifluoronitrosomethane, with sulfonyl fluoride vinyl ether, with carbalkoxyperfluoroalkoxyvinyl ether, polychlorotrifluoroethylene, polyvinyl fluoride, polyvinylidene fluoride, polyacrolein, polyacrylamide, polyacrylonitrile, polycyanoacrylates, polymethacrylimide, cycloolefinic copolymers, in particular ones derived from norbornene; polymers having C-O bonds in the main chain, for example polyacetal, polyoxymethylene, polyether, polypropylene oxide, polyepichlorohydrin, polytetrahydrofuran, polyphenylene oxide, polyether ketone, polyesters, in particular polyhydroxyacetic acid, polyethylene terephthalate, polybutylene terephthalate, polyhydroxybenzoate, polyhydroxypropionic acid, polypivalolactone, polycaprolactone, polymalonic acid, polycarbonate;
- polymers having C-S bonds in the main chain, for example polysulfide ether, polyphenylene sulfide, polyether sulfone;

polymeric C-N bonds in the backbone, for example

polyimines, polyisocyanides, polyetherimine, polyaniline, polyamides, polyhydrazides, polyurethanes, polyimides, polyazoles, polyazines;

- liquid crystalline polymers, in particular Vectra, as well as

inorganic polymers, such as polysilanes, polycarbosilanes, polysiloxanes, polysilicic acid, polysilicates, silicones, polyphosphazenes and polythiazyl.

Furthermore, the polymers (B) also comprise polymers having covalently bound acid groups. These acid groups encompass, in particular, sulfonic acid groups.

- The polymers modified with sulfonic acid groups preferably have a content of

sulfonic acid groups in the range from 0.5 to 3 meq/g. This value is determined via the ion exchange capacity (IEC).

To measure the IEC, the sulphonic acid groups are converted to the free acid. To this end, the polymer is treated in a known way with acid, removing excess acid by washing. Thus, the sulphonated polymer is initially treated for 2 hours in boiling water. Subsequently, excess water is dabbed off and the sample is dried at 160°C in a vacuum drying cabinet at  $p < 1$  mbar for 15 hours. Then, the dry weight of the membrane is determined. The polymer thus dried is then dissolved in DMSO at 80°C for 1h. Subsequently, the solution is titrated with 0.1M NaOH. The ion exchange capacity (IEC) is then calculated from the consumption of acid to the equivalence point and the dry weight.

Such polymers are known to those skilled in the art. Thus, polymers containing sulfonic acid groups can be prepared, for example, by sulfonation of polymers. Processes for the sulfonation of polymers are described in F. Kucera et al., Polymer Engineering and Science 1988, Vol. 38, No. 5, 783-792. In this connection, the sulfonation conditions can be chosen such that a low degree of sulfonation develops (DE-A-19959289).

A further class of nonfluorinated polymers obtained by sulfonation of high-temperature-stable thermoplastics has been developed in this way. Thus, sulfonated polyether ketones (DE-A-4219077, WO96/01177), sulfonated polysulfones (J. Membr. Sci. 83 (1993) p. 211) or sulfonated polyphenylene sulfide (DE-A-19527435) are known.

US-A-6110616 describes copolymers of butadiene and styrene and their subsequent sulfonation for use in fuel cells.

Furthermore, such polymers can also be obtained by polyreactions of monomers which comprise acid groups. Thus, perfluorinated polymers as described in US-A-5422411 can be produced by copolymerisation of trifluorostyrene and sulphonyl-modified trifluorostyrene.

These perfluorosulfonic acid polymers include, inter alia, Nafion® (US-A-3692569). This polymer can, as described in US-A-4453991, be brought into

solution and then used as ionomer.

Preferred polymers having acid groups include, inter alia, sulfonated polyether ketones, sulfonated polysulfones, sulfonated polyphenylene sulfides, perfluorinated polymers containing sulfonic acid groups, as described in US-A-  
5 3692569, US-A-5422411 and US-A-6110616.

For use in fuel cells having a long-term operating temperature above 100°C, preference is given to polymers (B) which have a glass transition temperature or Vicat softening temperature VST/A/50 of at least 100°C, preferably at least 150°C and very particularly preferably at least 180°C. Here, preference is given to  
10 polysulphones with a Vicat softening temperature VST/A/50 of 180°C to 230°C.

In addition, preference is given to polymers (B) which have a low solubility in phosphoric acid and/or are not degraded substantially by phosphoric acid. In a particular embodiment of the present invention, the weight decreases only insignificantly as a result of a treatment with 85% strength phosphoric acid. The  
15 weight ratio of the plate after the phosphoric acid treatment to the weight of the plate before the treatment is preferably greater than or equal to 0.8, in particular greater than or equal to 0.9 and particularly preferably greater than or equal to 0.95. This value is determined on a plate of polymer (B) which is 2 mm thick, 5 cm long and 2 cm wide. This plate is placed in phosphoric acid, with the weight ratio of  
20 phosphoric acid to the plate being 10. The phosphoric acid is subsequently heated at 100°C for 24 hours while stirring. The plate is subsequently freed of excess phosphoric acid by washing with water and dried. The plate is then weighed again.

The preferred polymers include polysulphones, in particular polysulphone having aromatic groups in the backbone. In a particular embodiment of the present  
25 invention, preferred polysulfones and polyether sulfones have a melt flow rate MVR 300/21.6 of less than or equal to 40 cm<sup>3</sup>/10 min, in particular less than or equal to 30 cm<sup>3</sup>/10 min and particularly preferably less than or equal to 20 cm<sup>3</sup>/10 min, measured in accordance with ISO 1133.

The mixture obtained in step A) is, in step B), heated to a temperature of up to  
30 400°C, in particular 350°C, preferably up to 280°C, in particular from 100°C to 250°C and particularly preferably the range from 200°C to 250°C. An inert gas, for

example nitrogen or a noble gas such as neon, argon, is used here.

Furthermore, it has been found that when using aromatic dicarboxylic acids (or heteroaromatic dicarboxylic acids) such as isophthalic acid, terephthalic acid, 2,5-dihydroxyterephthalic acid, 4,6-dihydroxyisophthalic acid, 2,6-dihydroxyisophthalic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, bis(4-carboxyphenyl) ether, benzophenone-4,4'-dicarboxylic acid, bis(4-carboxyphenyl) sulfone, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazole-dicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, the temperature in step B) is advantageously in the range up to 300°C, preferably from 100°C to 250°C.

In one variant of the process, the heating according to step B) can be carried out after the formation of a sheet-like structure according to step C).

The mixture prepared in step A) and/or step B) can further comprise organic solvents. These can have a positive influence on the processability. For example, the rheology of the solution can be improved in this way, so that it can be extruded or spread by means of a doctor blade more easily.

To improve the properties in terms of application technology further, fillers, in particular proton-conducting fillers, and additional acids can additionally be added to the membrane. The addition can be carried out, for example, in step A), step B) and/or step C). Furthermore, these additives can, if they are in liquid form, also be added after the polymerization in step D).

Non-limiting examples of proton-conducting fillers are

25	sulphates, such as	CsHSO <sub>4</sub> , Fe(SO <sub>4</sub> ) <sub>2</sub> , (NH <sub>4</sub> ) <sub>3</sub> H(SO <sub>4</sub> ) <sub>2</sub> , LiHSO <sub>4</sub> , NaHSO <sub>4</sub> , KHSO <sub>4</sub> , RbSO <sub>4</sub> , LiN <sub>2</sub> H <sub>5</sub> SO <sub>4</sub> , NH <sub>4</sub> HSO <sub>4</sub> ,
30	phosphates, such as	Zr <sub>3</sub> (PO <sub>4</sub> ) <sub>4</sub> , Zr(HPO <sub>4</sub> ) <sub>2</sub> , HZr <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> , UO <sub>2</sub> PO <sub>4</sub> ·3H <sub>2</sub> O, H <sub>8</sub> UO <sub>2</sub> PO <sub>4</sub> , Ce(HPO <sub>4</sub> ) <sub>2</sub> , Ti(HPO <sub>4</sub> ) <sub>2</sub> , KH <sub>2</sub> PO <sub>4</sub> , NaH <sub>2</sub> PO <sub>4</sub> , LiH <sub>2</sub> PO <sub>4</sub> , NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> , CsH <sub>2</sub> PO <sub>4</sub> , CaHPO <sub>4</sub> , MgHPO <sub>4</sub> , H <sub>3</sub> SbP <sub>2</sub> O <sub>8</sub> , H <sub>3</sub> Sb <sub>3</sub> P <sub>2</sub> O <sub>14</sub> , H <sub>5</sub> Sb <sub>5</sub> P <sub>2</sub> O <sub>20</sub> ,

- polyacid, such as  $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$  ( $n=21-29$ ),  $\text{H}_3\text{SiW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$  ( $n=21-29$ ),  $\text{H}_x\text{WO}_3$ ,  $\text{HSbWO}_6$ ,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ,  $\text{H}_2\text{Sb}_4\text{O}_{11}$ ,  $\text{HTaWO}_6$ ,  $\text{HNbO}_3$ ,  $\text{HTiNbO}_5$ ,  $\text{HTiTaO}_5$ ,  $\text{HSbTeO}_6$ ,  $\text{H}_5\text{Ti}_4\text{O}_9$ ,  $\text{HSbO}_3$ ,  $\text{H}_2\text{MoO}_4$ .
- 5 selenites and arsenides such as  $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$ ,  $\text{UO}_2\text{AsO}_4$ ,  $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$ ,  $\text{KH}_2\text{AsO}_4$ ,  $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ ,  $\text{Rb}_3\text{H}(\text{SeO}_4)_2$ ,
- oxides, such as  $\text{Al}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5$ ,  $\text{ThO}_2$ ,  $\text{SnO}_2$ ,  $\text{ZrO}_2$ ,  $\text{MoO}_3$
- silicates, such as zeolites, zeolites( $\text{NH}_4^+$ ), phyllosilicates, tectosilicates, H-natrolites, H-mordenites,  $\text{NH}_4$ -analclines,  $\text{NH}_4^-$
- 10 sodalites,  $\text{NH}_4^-$ -gallates, H-montmorillonites
- acids, such as  $\text{HClO}_4$ ,  $\text{SbF}_5$ ,
- fillers, such as carbides, in particular  $\text{SiC}$ ,  $\text{Si}_3\text{N}_4$ , fibres, in particular glass fibres, glass powders and/or polymer fibres, preferably based on polyazoles.
- 15 These additives can be present in the proton-conducting polymer membrane in customary amounts, but the positive properties such as high conductivity, long life and high mechanical stability of the membrane should not be impaired too greatly by addition of excessively large amounts of additives. In general, the membrane after the treatment according to step D) comprises not more than 80% by weight,
- 20 preferably not more than 50% by weight and particularly preferably not more than 20% by weight, of additives.
- In addition, this membrane can further comprise perfluorinated sulfonic acid additives (preferably 0.1-20% by weight, more preferably 0.2-15% by weight, very particularly preferably 0.2-10% by weight). These additives result in an
- 25 improvement in performance, to an increase in oxygen solubility and oxygen diffusion in the vicinity of the cathode and to a reduction in adsorption of phosphoric acid and phosphate onto platinum. (Electrolyte additives for phosphoric acid fuel cells. Gang, Xiao; Hjuler, H. A.; Olsen, C.; Berg, R. W.; Bjerrum, N. J. Chem. Dep. A, Tech. Univ. Denmark, Lyngby, Den. J. Electrochem. Soc.
- 30 (1993), 140(4), 896-902 and Perfluorosulfonimide as an additive in phosphoric

acid fuel cell. Razaq, M.; Razaq, A.; Yeager, E.; DesMarteau, Darryl D.; Singh, S. Case Cent. Electrochem. Sci., Case West. Reserve Univ., Cleveland, OH, USA. J. Electrochem. Soc. (1989), 136(2), 385-90.) Non-limiting examples of persulphonated additives are:

- 5 trifluoromethanesulphonic acid, potassium trifluoromethanesulphonate, sodium trifluoromethanesulphonate, lithium trifluoromethanesulphonate, ammonium trifluoromethanesulphonate, potassium perfluorohexanesulphonate, sodium perfluorohexanesulphonate, lithium perfluorohexanesulphonate, ammonium perfluorohexanesulphonate, perfluorohexanesulphonic acid, potassium  
10 nonafluorobutanesulphonate, sodium nonafluorobutanesulphonate, lithium nonafluorobutanesulphonate, ammonium nonafluorobutanesulphonate, cesium nonafluorobutanesulphonate, triethylammonium perfluorohexasulphonate, perfluorosulphonimides and Nafion.

- The formation of the sheet-like structure in step C) is effected by means of  
15 measures known per se from the prior art for polymer film production (casting, spraying, spreading by doctor blade, extrusion). Every support that is considered as inert under the conditions is suitable as a support. The supports include, in particular, films of polyethylene terephthalate (PET), polytetrafluoroethylene (PTFE), polyhexafluoropropylene, copolymers of PTFE with hexafluoropropylene,  
20 polyimides, polyphenylene sulfides (PPS) and polypropylene (PP).

To adjust the viscosity, the solution can, if appropriate, be admixed with a volatile organic solvent. Thus, the viscosity can be adjusted to the desired value and the formation of the membrane be facilitated.

- The thickness of the sheet-like structure obtained according to step C) is  
25 preferably from 10 to 4000  $\mu\text{m}$ , more preferably from 15 to 3500  $\mu\text{m}$ , in particular from 20 to 3000  $\mu\text{m}$ , particularly preferably from 30 to 1500  $\mu\text{m}$  and very particularly preferably from 50 to 1200  $\mu\text{m}$ .

- The treatment of the membrane in step D) is carried out, in particular, at temperatures in the range from 0°C to 150°C, preferably at temperatures from  
30 10°C to 120°C, in particular from room temperature (20°C) to 90°C, in the



presence of moisture or water and/or water vapor. The treatment is preferably performed at normal pressure, but can also be carried out with action of pressure. It is important that the treatment is carried out in the presence of sufficient moisture, as a result of which the polyphosphoric acid present is partially hydrolyzed to form  
5 low molecular weight polyphosphoric acid and/or phosphoric acid and thus contributes to strengthening of the membrane.

The partial hydrolysis of the polyphosphoric acid in step D) leads to strengthening of the membrane and to a decrease in the layer thickness and formation of a membrane. The strengthened membrane generally has a thickness in the range  
10 from 15 to 3000  $\mu\text{m}$ , preferably from 20 to 2000  $\mu\text{m}$ , in particular from 20 to 1500  $\mu\text{m}$ , with the membrane being self-supporting.

The upper temperature limit for the treatment in accordance with step D) is typically 150°C. With extremely short action of moisture, for example from overheated steam, this steam can also be hotter than 150°C. The duration of the  
15 treatment is substantial for the upper limit of the temperature.

The partial hydrolysis (step D) can also take place in climatic chambers where the hydrolysis can be specifically controlled with defined moisture action. In this connection, the moisture can be specifically set via the temperature or saturation of the surrounding area in contact with it, for example gases such as air, nitrogen,  
20 carbon dioxide or other suitable gases, or steam. The duration of the treatment depends on the parameters chosen as aforesaid.

Furthermore, the duration of the treatment depends on the thickness of the membrane.

Typically, the duration of the treatment amounts to between a few seconds to  
25 minutes, for example with the action of overheated steam, or up to whole days, for example in the open air at room temperature and lower relative humidity. Preferably, the duration of the treatment is between 10 seconds and 300 hours, in particular 1 minute to 200 hours.

If the partial hydrolysis is performed at room temperature (20°C) with ambient air  
30 having a relative humidity of 40-80%, the duration of the treatment is between 1

and 200 hours.

The membrane obtained in accordance with step D) can be formed in such a way that it is self-supporting, i.e. it can be detached from the support without any damage and then directly processed further, if applicable.

- 5 The concentration of phosphoric acid and thus the conductivity of the polymer membrane of the invention can be set via the degree of hydrolysis, i.e. the duration, temperature and ambient humidity. According to the invention, the concentration of phosphoric acid is reported as mol of acid per mol of repeating units in the polymer. For the purposes of the present invention, a concentration  
10 (mol of phosphoric acid per mol of repeating units of the formula (III), i.e. polybenzimidazole) of from 10 to 80, in particular from 12 to 60, is preferred. Such high degrees of doping (concentrations) can be obtained only with difficulty, if at all, by doping of polyazoles with commercially available ortho-phosphoric acid.

- Subsequent to the treatment according to step D) the membrane can be  
15 crosslinked by action of heat in the presence of oxygen. This hardening of the membrane effects an additional improvement in the properties of the membrane. To this end, the membrane can be heated to a temperature of at least 150°C, preferably at least 200°C and particularly preferably at least 250°C. The oxygen concentration in this process step is usually in the range from 5 to 50% by volume,  
20 preferably from 10 to 40% by volume, without this constituting a restriction.

- The cross-linking can also take place by action of IR or NIR (IR = infrared, i.e. light having a wavelength of more than 700 nm; NIR = near-IR, i.e. light having a wavelength in the range of about 700 to 2000 nm and an energy in the range of about 0.6 to 1.75 eV), respectively. Another method is  $\beta$ -ray irradiation. In this  
25 connection, the irradiation dose is between 5 and 200 kGy.

Depending on the degree of cross-linking desired, the duration of the cross-linking reaction can be within a wide range. In general, this reaction time is in the range from 1 second to 10 hours, preferably from 1 minute to 1 hour, without this constituting a restriction.

- 30 The polymer membrane according to the invention has improved material

properties compared to the doped polymer membranes previously known. In particular, they exhibit better performances in comparison with known doped polymer membranes. The reason for this is in particular an improved proton conductivity. This is at least 0.1 S/cm, preferably at least 0.11 S/cm, in particular at least 0.12 S/cm at temperatures of 120°C. If the membranes of the invention comprise polymers having sulfonic acid groups, the membranes display a high conductivity even at a temperature of 70°C. The conductivity is dependent, inter alia, on the sulfonic acid group content of the membrane. The higher this proportion, the better the conductivity at low temperatures. A membrane according to the invention can be moistened at low temperatures. For this purpose, the compound used as energy source, for example hydrogen, can, for example, be provided with a proportion of water. However, the water formed by the reaction is in many cases sufficient to achieve moistening.

The specific conductivity is measured by means of impedancy spectroscopy in a 4-pole arrangement in potentiostatic mode and using platinum electrodes (wire, diameter of 0.25 mm). The distance between the current-collecting electrodes is 2 cm. The spectrum obtained is evaluated using a simple model comprising a parallel arrangement of an ohmic resistance and a capacitor. The cross-section of the specimen of the membrane doped with phosphoric acid is measured immediately before mounting the specimen. To measure the temperature dependency, the measurement cell is brought to the desired temperature in an oven and regulated using a Pt-100 thermocouple arranged in the immediate vicinity of the specimen. After the temperature has been reached, the specimen is kept at this temperature for 10 minutes before beginning the measurement.

In a particular embodiment of the present invention, the membranes have a high mechanical stability. This parameter is given by the hardness of the membrane which is determined by means of microhardness measurement in accordance with DIN 50539. For this purpose, the membrane is gradually loaded with a Vickers diamond up to a force of 3 mN over a period of 20 s and the penetration depth is determined. According to this, the hardness at room temperature is at least 5 mN/mm<sup>2</sup>, preferably at least 50 mN/mm<sup>2</sup> and very particularly preferably at least 200 mN/mm<sup>2</sup>, without this constituting a restriction. The force is subsequently kept

constant at 3 mN for 5 s and the creep is calculated from the penetration depth. In the case of preferred membranes, the creep  $C_{HU}$  0.003/20/5 under these conditions is less than 30%, preferably less than 15% and very particularly preferably less than 5%. The modulus determined by means of microhardness measurement YHU is at least 0.1 MPa, in particular at least 2 MPa and very particularly preferably at least 5 MPa, without this constituting a restriction.

Possible fields of use of the polymer membranes of the invention include, inter alia, use in fuel cells, in electrolysis, in capacitors and in battery systems.

The present invention also relates to a membrane electrode unit which includes at least one polymer membrane according to the invention. For further information on membrane-electrode units, reference may be made to the specialist literature, in particular the patents US-A-4,191,618, US-A-4,212,714 and US-A-4,333,805. The disclosure of the abovementioned references [US-A-4,191,618, US-A-4,212,714 and US-A-4,333,805] in respect of the structure and the production of membrane-electrode units and also the electrodes, gas diffusion layers and catalysts to be selected is incorporated by reference into the present description.

In a variant of the present invention, the membrane formation can also be performed directly on the electrode rather than on a support. Through this, the treatment in accordance with step D) can be correspondingly shortened since it is no longer required for the membrane to be self-supporting. Such a membrane is also an object of the present invention.

Another object of the present invention is an electrode provided with a proton-conducting polymer coating comprising polyazole blends obtained by a process comprising the steps

A) preparation of a mixture comprising

polyphosphoric acid,

at least one polyazole (polymer A) and/or one or more compounds which are suitable for forming polyazoles under the action of heat according to step B),

- B) heating of the mixture obtainable according to step A) under inert gas to temperatures of up to 400°C,
- C) application of a layer using the mixture from step A) and/or B) to an electrode,

- 5 D) treatment of the membrane formed in step C),

with at least one further polymer (polymer B) which is not a polyazole being added to the composition obtainable according to step A) and/or step B) and the weight ratio of polyazole to polymer B is in the range from 0.05 to 10.

- 10 For the sake of completeness, it may be noted that all preferred embodiments of a self-supporting membrane apply analogously for a membrane applied directly to the electrode.

In a particular embodiment of the present invention, the coating has a thickness of from 2 to 3000  $\mu\text{m}$ , preferably from 2 to 2000  $\mu\text{m}$ , in particular from 3 to 1500  $\mu\text{m}$ ,  
15 particularly preferably from 5 to 500  $\mu\text{m}$  and very particularly preferably from 10 to 200  $\mu\text{m}$ , without being limited to this.

The treatment according to step D) leads to a hardening of the coating. The treatment is carried out until the coating has a hardness which is sufficient for it to be pressed to produce a membrane-electrode unit. A sufficient hardness is  
20 ensured when a membrane treated in this way is self-supporting. However, a lower hardness is sufficient in many cases. The hardness determined in accordance with DIN 50539 (microhardness measurement) is generally at least 1  $\text{mN/mm}^2$ , preferably at least 5  $\text{mN/mm}^2$  and very particularly preferably at least 50  $\text{mN/mm}^2$ , without being limited to this.

- 25 An electrode which has been coated in this way can be installed in a membrane-electrode unit which, if appropriate, has at least one polymer membrane according to the invention.

In a further variant, a catalytically active layer can be applied to the membrane according to the invention and this catalytically active layer can be joined to a gas

diffusion layer. For this purpose, a membrane is formed according to steps A) to D) and the catalyst is applied.

Furthermore, the formation of the membrane according to steps A) to D) can also be carried out on a support or a support film which already has the catalyst. After  
5 removal of the support or the support film, the catalyst is located on the membrane according to the invention. These structures are also object of the present invention.

Likewise, a membrane-electrode unit is object of the present invention which has at least one coated electrode and/or at least one polymer membrane according to  
10 the invention in combination with a further polymer membrane based on polyazoles or a polymer blend membrane comprising at least one polymer based on polyazoles.

## Claims

1. A proton-conducting polymer membrane containing polyazole blends and is obtainable by a process comprising the steps
  - A) preparation of a mixture comprising  
5 polyphosphoric acid,  
  
at least one polyazole (polymer A) and/or one or more compounds which are suitable for forming polyazoles under the action of heat according to step B),  
  
B) heating of the mixture obtainable according to step A) under inert gas to  
10 temperatures of up to 400°C,  
  
C) application of a layer using the mixture from step A) and/or B) to a support,  
  
D) treatment of the membrane formed in step C) until it is self-supporting, with at least one further polymer (polymer B) which is not a polyazole being added to the composition obtainable according to step A) and/or step B)  
15 and the weight ratio of polyazole to polymer B is in the range from 0.1 to 50.
2. The membrane as claimed in claim 1, characterized in that the mixture prepared in step A) comprises compounds which are suitable for forming polyazoles under the action of heat in step B), with these compounds  
20 comprising one or more aromatic and/or heteroaromatic tetraamino compounds and one or more aromatic and/or heteroaromatic carboxylic acids or derivatives thereof which have at least two acid groups per carboxylic acid monomer and/or one or more aromatic and/or heteroaromatic diaminocarboxylic acids.
- 25 3. The membrane as claimed in claim 1, characterized in that the mixture prepared in step A) comprises compounds which are suitable for forming polyazoles under the action of heat in step B), with these compounds being obtainable by reaction of one or more aromatic and/or

heteroaromatic tetraamino compounds with one or more aromatic and/or heteroaromatic carboxylic acids or derivatives thereof which have at least two acid groups per carboxylic acid monomer or of one or more aromatic and/or heteroaromatic diaminocarboxylic acids in the melt at temperatures of up to 400°C.

4. The membrane as claimed in claim 2 or 3, characterized in that aromatic and/or heteroaromatic tetraamino compounds used as compounds suitable for forming polyazoles comprise compounds selected from the group consisting of 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine and 1,2,4,5-tetraaminobenzene.

5. The membrane as claimed in claim 2, 3 or 4, characterized in that aromatic and/or heteroaromatic carboxylic acids or derivatives thereof having at least two acid groups per carboxylic acid monomer used as compounds suitable for forming polyazoles comprise compounds selected from the group consisting of isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dihydroxyisophthalic acid, 2,3-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, bis(4-carboxyphenyl) ether, benzophenone-4,4'-dicarboxylic acid, bis(4-dicarboxyphenyl) sulfone, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid, or their C1-C20-alkyl esters or C5-C12-aryl esters, or their acid anhydrides or acid chlorides.

6. The membrane as claimed in claim 2, 3, 4 or 5, characterized in that the compounds suitable for forming polyazoles comprise aromatic tricarboxylic



acids, their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid halides or tetracarboxylic acids, their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid halides.

- 5 7. The membrane as claimed in claim 6, characterized in that the aromatic tricarboxylic acids comprise compounds selected from the group consisting of 1,3,5-benzenetricarboxylic acid (trimesic acid); 2,4,5-benzenetricarboxylic acid (trimellitic acid); (2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphenyltricarboxylic acid; 3,5,4'-biphenyltricarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acid; 10 naphthalene-1,4,5,8-tetracarboxylic acid, 3,5,3',5'-biphenyltetracarboxylic acid, benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid and 1,4,5,8-naphthalenetetracarboxylic acid.
- 15 8. The membrane as claimed in claim 6 or 7, characterized in that the content of tricarboxylic acid and/or tetracarboxylic acids is from 0 to 30 mol%, preferably from 0.1 to 20 mol%, in particular from 0.5 to 10 mol%, based on dicarboxylic acid used.
- 20 9. The membrane as claimed in one or more of claims 2 to 8, characterized in that the compounds suitable for forming polyazoles comprise heteroaromatic dicarboxylic acids, tricarboxylic acids and/or tetracarboxylic acids which contain at least one nitrogen, oxygen, sulfur or phosphorus atom in the aromatics.
- 25 10. The membrane as claimed in claim 9, characterized in that pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid, and also their C1-C20-alkyl esters or C5-C12-aryl 30 esters, or their acid anhydrides or their acid chlorides are used.
11. The membrane as claimed in claim 2 or 3, characterized in that the

compounds suitable for forming polyazoles comprise diaminobenzoic acid and/or its monohydrochloride and dihydrochloride derivatives.

12. The membrane as claimed in claim 1, characterized in that the polymer B) is used in step A) in an amount in the range from 10 to 50% by weight, based on the weight of the mixture A) and/or B).
13. The membrane as claimed in claim 1, characterized in that the polymer B) comprises at least one polyolefin.
14. The membrane as claimed in claim 1, characterized in that the polymer B) comprises at least one polymer having C-O bonds.
15. The membrane as claimed in claim 1, characterized in that the polymer B) comprises at least one polymer having C-S bonds.
16. The membrane as claimed in claim 1, characterized in that the polymer B) comprises at least one polymer having C-N bonds.
17. The membrane as claimed in claim 1, characterized in that the polymer B) comprises at least one inorganic polymer.
18. The membrane as claimed in claim 1, characterized in that the polymer B) comprises at least one sulfonated polymer.
19. The membrane as claimed in one or more of the preceding claims, characterized in that the heating according to step B) is carried out after the formation of a sheet-like structure according to step C).
20. The membrane as claimed in claim 1, characterized in that the treatment according to step D) is carried out at temperatures in the range from 0°C to 150°C in the presence of moisture.
21. The membrane as claimed in claim 1, characterized in that the treatment of the membrane in step D) is carried out for from 10 seconds to 300 hours.
22. The membrane as claimed in claim 1, characterized in that the membrane

formed after step D) is crosslinked by action of oxygen.

23. The membrane as claimed in claim 1, characterized in that a layer having a thickness of from 20 to 4000  $\mu\text{m}$  is produced in step C).

24. The membrane as claimed in claim 1, characterized in that the membrane formed after step D) has a thickness of from 15 to 3000  $\mu\text{m}$ .

25. An electrode provided with a proton-conducting polymer coating which comprises polyazole blends and is obtained by a process comprising the steps

A) preparation of a mixture comprising

polyphosphoric acid,

at least one polyazole (polymer A) and/or one or more compounds which are suitable for forming polyazoles under the action of heat according to step B),

B) heating of the mixture obtainable according to step A) under inert gas to temperatures of up to 400°C,

C) application of a layer using the mixture from step A) and/or B) to an electrode,

D) treatment of the membrane formed in step C),

with at least one further polymer (polymer B) which is not a polyazole being added to the composition obtainable according to step A) and/or step B) and the weight ratio of polyazole to polymer B is in the range from 0.1 to 50.

26. The electrode as claimed in claim 24, wherein the coating has a thickness of from 2 to 3000  $\mu\text{m}$ .

27. A membrane electrode unit containing at least one electrode and at least one membrane according to one or more of claims 1 to 24.

28. The membrane electrode unit containing at least one electrode according to claim 25 or claim 26 and at least one membrane according to one or more of claims 1 to 24.
29. A fuel cell containing one or more membrane electrode units according to claim 27 or claim 28.

## Abstract

Proton-conducting polymer membrane comprising polyazole blends and its application in fuel cells

The present invention relates to a proton-conducting polymer membrane which  
5 comprises polyazole blends and is obtainable by a process comprising the steps

A) preparation of a mixture comprising

polyphosphoric acid,

10 at least one polyazole (polymer A) and/or one or more compounds which are suitable for forming polyazoles under the action of heat according to step B),

B) heating of the mixture obtainable according to step A) under inert gas to temperatures of up to 400°C,

C) application of a layer using the mixture from step A) and/or B) to a support,

15 D) treatment of the membrane formed in step C) until it is self-supporting, with at least one further polymer (polymer B) which is not a polyazole being added to the composition obtainable according to step A) and/or step B) and the weight ratio of polyazole to polymer B is in the range from 0.1 to 50.

